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(71) Applicant (for all designated States except US): REXAM INDUSTRIES CORP. [US/US]; Suite 340, 4201 Congress Street, Charlotte, NC 28209 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): FIELDS, Randall, Thomas [US/US]; 6609 Silver Fox Road, Charlotte, NC 28270 (US).  
HUFFER, Scott [US/US]; 3060 Crestview lane, Lancaster, SC 29720 (US).

(74) Agents: HUMPHREY, Christopher, M. et al.; Alston &amp; Bird LLP, P.O. Drawer 34009, Charlotte, NC 28234-4009 (US).

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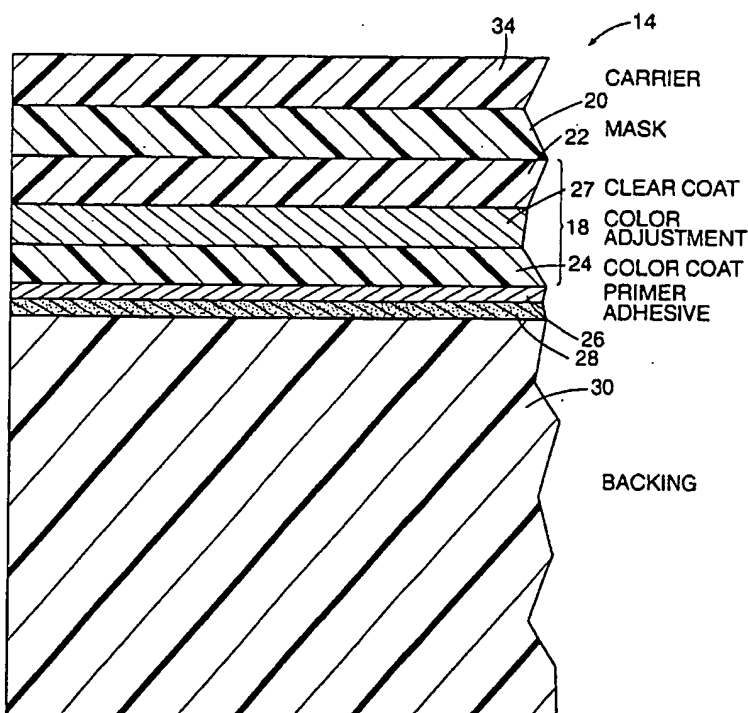
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(54) Title: MIGRATORY ADDITIVES FOR MASK LAYER OF DECORATIVE SHEET MATERIAL

## (57) Abstract

The flexible, weatherable decorative sheet material provided by the present invention comprises a thermoformable decorative paint film having an inner surface and a weatherable outer surface suitable for forming an exterior finish for a part, such as an automobile body part. The sheet material further includes an extensible mask layer releasably adhered to the outer surface of the paint film to form a protective film overlying the paint film. The mask layer comprises a polyurethane, polyolefin, polyester, or polyamide composition and includes at least one migratory additive designed to migrate to the clear coat layer of the paint film or to prevent migration of additives from the mask layer to the clear coat. Migratory additives suitable for use with the present invention include, but are not limited to, hardness enhancers, release agents, ultraviolet light stabilizers, antioxidants, dyes, lubricants, surfactants, catalysts, slip additives and mixtures thereof. A method of constructing the decorative sheet material and a composite shaped part including the decorative sheet material are also provided.



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## MIGRATORY ADDITIVES FOR MASK LAYER OF DECORATIVE SHEET MATERIAL

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### FIELD OF THE INVENTION

The present invention relates to sheet materials generally and more particularly relates to a sheet material suitable for use as a flexible, weatherable paint film.

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### BACKGROUND OF THE INVENTION

Manufacturers have shown increasing interest in using paint films in lieu of spray painting for providing a decorative surface finish for parts, such as automobile body parts. This manufacturing technique reduces the environmental concerns associated with painting and has the potential to reduce manufacturing costs. An automobile body part utilizing a plastic paint film to provide a high quality base coat/clear coat automotive finish is disclosed, for example, in U.S. Patent No. 4,810,540, which is incorporated by reference herein in its entirety. In producing the part, the paint film is typically formed into a contoured three-dimensional configuration corresponding to the shape of the outer surface of the part by suitable methods, such as by thermoforming.

Automobile manufacturers, for example, require that automotive parts have an exterior paint appearance that meets demanding performance and appearance specifications, such as weatherability, resistance to ultraviolet light degradation, high gloss and high distinctness-of-image (DOI). These stringent requirements are met, in part, by the addition of certain additives, such as ultraviolet light stabilizers, to the clear coat layer. Some of these additives are most effective when present at the outer, exposed surface of the clear coat layer. However, preparing a clear coat formulation containing a non-uniform distribution of an additive can present processing difficulties. There remains a need for a method of preparing a paint film wherein additives to the clear coat layer are distributed in an effective manner.

## SUMMARY OF THE INVENTION

The decorative sheet material of the present invention includes a mask layer having additives designed to either migrate into the clear coat layer to enhance weatherability or other desirable properties of the clear coat layer or to prevent migration of additives from the clear coat into the mask layer. Using the mask layer of the present invention, performance and appearance properties of the clear coat are enhanced because performance-enhancing additives in the clear coat layer are prevented from migrating into the adjacent mask layer. The mask layer of the present invention also provides an efficient mechanism for transferring additives into the clear coat layer, particularly additives that perform more efficiently when placed primarily in the outer surface region of the clear coat, rather than distributed uniformly throughout the clear coat layer.

The present invention provides a flexible, weatherable decorative sheet material that includes a decorative paint film and an extensible mask releasibly adhered to the outer surface of the paint film to form a protective film overlying the paint film, wherein the mask comprises a film-forming polymer composition containing at least one migratory additive. Preferably, the migratory additive is selected from the group consisting of hardness enhancers, release agents, ultraviolet light stabilizers and antioxidants, dyes, lubricants, surfactants, catalysts, slip additives and mixtures thereof.

Dyes useful as migratory additives include fluorescing agents. The dye may be printed on the mask layer in the form of a graphic design using a process selected from the group consisting of gravure, rotary screen, flatbed step-and-repeat screen, ink jet and flexographic printing techniques. At least a portion of the dye will transfer from the mask layer to the clear coat, thereby transferring the graphic design to the clear coat layer.

The migratory additive may also comprise an ultraviolet light stabilizer, such as triazoles, triazines, and benzophenone. Preferably, the ultraviolet light stabilizer comprises benzotriazole. In one embodiment, the migratory additive includes at least one benzotriazole ultraviolet light stabilizer and at least one hindered amine ultraviolet light stabilizer.

The migratory additive may also be a release agent, such as a wax or a silicone. The release agent is designed to impart a reduced coefficient friction to the outer surface of the paint film. Additionally, the migratory additive may be a catalyst, such as para-toluenesulfonic acid.

5       The paint film may comprise a single layer of a pigmented polymer or a clear coat layer of a transparent weatherable polymer and an underlying color coat layer of a pigmented polymer. The sheet material may also include a thermoformable backing layer bonded to the inner surface of the paint film and an adhesive layer affixing the paint film to the backing layer.

10       The present invention also provides a method of making a flexible, weatherable decorative sheet material. The method includes the step of applying a coating comprising a film-forming polymer containing at least one migratory additive composition onto a casting surface. The coating is then dried to form a continuous polymer mask releasably adhered to the casting surface. A decorative  
15       paint film is formed having an inner surface and an outer surface and the outer surface of the paint film is releasably bonded to the exposed surface of the mask to form a composite laminate. The laminate is then heated to effect migration of the migratory additive into the paint film. Thereafter, the mask may be stripped from the paint film to expose the outer surface of the paint film.

20       The heating step described above may be accomplished by thermoforming the decorative sheet material into a three-dimensional shape while the mask layer remains in place. Thereafter, the thermoformed decorative sheet material may be placed in an injection mold with the mask layer facing the mold surface. A molten thermoplastic polymer may be injected into the mold where it hardens and  
25       bonds to the decorative sheet material to form a composite shaped part. In another embodiment, the decorative sheet material is placed in a mold, such as a compression mold, injection mold, or blow mold, in the form of a substantially flat sheet without thermoforming the sheet material beforehand. In that embodiment, the heating of the mold effects migration of the migratory additive  
30       into the paint film.

## BRIEF DESCRIPTION OF THE DRAWINGS

Having thus described the invention in general terms, reference will now be made to the accompanying drawings, which are not necessarily drawn to scale, and wherein:

5        Figure 1 is a perspective view of an automobile illustrating the front fascia of the automobile having a decorative paint film applied thereto;

Figure 2 is a front view of an automobile front fascia having a decorative paint film applied thereto;

10       Figure 3 is a cross-sectional view of the fascia shown in Figure 2 taken along line 3-3 of Figure 2;

Figure 4 is a cross-sectional view of the decorative sheet material of the present invention adhered to a substrate;

Figure 5 is a cross-sectional view of the decorative sheet material of the present invention including a clear coat and a color coat layer;

15       Figure 6 is a cross-sectional view of the decorative sheet material of the present invention having a single paint film layer;

Figure 7 is a schematic illustration of a process for construction of the decorative sheet material of the present invention;

20       Figure 8 is a schematic illustration of a process for applying the mask layer to the outer surface of a decorative paint film;

Figures 9A-9D are schematic illustrations of the steps in a thermoforming process used to construct a preform; and

25       Figures 10A-10C are schematic illustrations of steps in an injection molding process for forming a composite shaped part.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention now will be described more fully hereinafter with reference to the accompanying drawings, in which preferred embodiments of the invention are shown. This invention may, however, be embodied in many  
30       different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will

be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. Like numbers refer to like elements throughout.

Figure 1 illustrates an automobile 10 having a composite shaped part 12. As shown, the composite shaped part 12 is a complex, contoured three-dimensional front fascia of the automobile 10. The composite shaped part 12 has a decorative sheet material 14 applied thereto. Although not limited to such applications, the decorative sheet material 14 of the present invention is particularly advantageous for providing a decorative surface on a composite shaped part 12 of an automobile 10. However, those skilled in the art will appreciate that the present invention could be used in a variety of applications requiring a weatherable, decorative surface.

Figure 2 is a front view of the composite shaped part 12 having the decorative sheet material 14 applied thereto. Figure 3 is a cross-sectional side view of the composite shaped part 12 comprising a substrate 16 having a decorative sheet material 14 applied thereto. As illustrated in Figure 3, the decorative sheet material 14 undergoes different amounts of elongation at different points along the contoured surface of the composite shaped part 12. In one embodiment, the decorative sheet material 14 of the present invention has a three-dimensional configuration in which certain areas of the sheet material have been subjected to elongation in excess of about 300%, and other areas of the sheet material are substantially non-elongated. However, the difference in gloss value between the elongated areas and the non-elongated areas should be no more than 10 gloss units with a minimum 60 degree gloss value of at least 60. The decorative sheet material 14 of the present invention is capable of maintaining a high level of gloss regardless of the amount of elongation experienced by the decorative sheet material during a thermoforming or molding process.

Figure 4 shows a greatly expanded cross-sectional view of a composite shaped part 12 comprising a decorative sheet material 14 of the present invention adhered to a substrate 16. The decorative sheet material includes a mask layer 20, a clear coat layer 22, a color coat layer 24, a primer layer 26, an adhesive layer 28, and a thermoformable backing layer 30.

The extensible mask layer 20 is designed to maintain gloss and DOI during forming processes and molding processes. Forming processes include, but are not limited to, thermoforming, cold stretching, and vacuum forming. Molding processes include, but are not limited to, injection molding, compression molding, and blow molding. The mask layer 20 also adds strength to the decorative sheet material 14 and improves process uniformity during the thermoforming process. Additionally, the extensible mask layer 20 protects the underlying layers of the decorative sheet material 14 from scratching or marring until the part is ready for display. The mask layer 20 is capable of stretching up to about 600 percent during thermoforming and has a room temperature elongation at break of at least about 200 percent.

The mask layer 20 may be retained as the outer layer of the decorative sheet material 14 during construction of the final product, such as an automobile. Thereafter, the mask layer 20 may be removed to reveal the underlying decorative paint film 18. For instance, the extensible mask layer 20 can be maintained as a protective layer and removed only after the vehicle has completed shipment and is ready for delivery to a customer. The extensible mask layer 20 is releasably bonded to the underlying decorative paint film 18 and may be stripped away from the underlying layers in a single piece. In a preferred embodiment, the mask layer 20 is transparent or substantially transparent to permit visual inspection of the part for surface defects without removal of the mask layer.

Additionally, the extensible mask layer 20 maintains high gloss and DOI during injection or compression molding, such as thermoplastic or thermoset compression molding, where the mold is roughened or deglossed. Roughened molds are less expensive than highly polished molds and are also functionally superior to highly polished molds because the rough mold surface enhances air removal from the mold as the mold closes. The extensible mask layer 20 protects the paint film 18 from loss of gloss or other damage caused by the mold without resorting to the use of highly polished molds.

Preferably, the extensible mask layer 20 is about 0.3 mils to about 3.0 mils in thickness. The extensible mask layer 20 comprises a polyurethane,



polyolefin, such as polyethylene or polypropylene, polyester, such as polyethylene terephthalate, or polyamide composition. Preferably, the mask layer 20 comprises a dried film of an aliphatic or aromatic polyester or polyether polyurethane in the form of an dispersion or a solution. For example, 5 polyurethane polymers QA 5218 and QA 5026, manufactured by Mace Adhesives and Coatings of Dudley, Massachusetts, may be used to form the mask layer 20. In one embodiment, the mask layer 20 comprises about 85 to about 99.5 weight percent polyurethane water-borne dispersion. Advantageously, a small amount of surfactant (about 0.05 to about 0.2 weight percent), such as 10 SURFYNOL 104H manufactured by Air Products of Allentown, PA, is added to lower surface tension.

The mask layer 20 composition may include additional additives designed to migrate into the clear coat layer 22 to enhance weatherability or other desirable properties of the clear coat layer or to prevent migration of additives from the 15 clear coat into the mask layer. The migratory additives also generally migrate to the exposed outer surface of the mask layer 20. Migratory additives suitable for use with the present invention include, but are not limited to, hardness enhancers, release agents, ultraviolet light stabilizers, antioxidants, dyes, lubricants, surfactants, including SURFYNOL surfactants, catalysts, including para-toluene 20 sulfonic acid (p-TSA), slip additives and mixtures thereof. The migratory additives are generally added in amounts ranging from about 0.01 to about 2.0 weight percent, with all additives accounting for no more than about 5.0 weight percent of the mask layer 20 composition.

Hardness enhancers suitable for use with the present invention include 25 cross-linking agents, such as a melamine or polyisocyanate. It is desirable for the clear coat 22 to be resistant to scratching and marring encountered during use of the composite part 12. One method of increasing scratch/mar resistance is by increasing clear coat hardness through polymer cross-linking. However, if the cross-linking agent is added to the clear coat 22, hardening of the paint film 18 30 may occur prior to thermoforming or molding, which would reduce the amount of elongation possible without damaging the film. The cross-linking agent may be placed in the mask layer 20 to prevent premature cross-linking. The heat of a

thermoforming or molding process triggers migration of the cross-linking agent into the clear coat, thereby initiating cross-linking with a polymer, such as LUMIFLON® fluoropolymer, found in the clear coat layer 22. Specific cross-linking agents suitable for use with the present invention include Cymel 303 and  
5 XAMA-7.

Dyes useful as a migratory additive include fluorescing agents, such as TINUVIN 1130 and TINUVIN 928. In one embodiment, the dye is printed on the mask layer 20 in the form of a graphic design or image. The dye may be printed on the mask layer 20 using printing methods such as gravure, rotary  
10 screen, flat bed step-and-repeat screen, ink jet, flexographic or other printing techniques. During the thermoforming and/or molding process, at least a portion of the dye migrates from the mask layer 20 to the clear coat layer 22, thereby transferring the graphic design or image to the decorative paint film 18.

Ultraviolet light stabilizers and antioxidants, such as hindered amine  
15 ultraviolet light stabilizers, may be added to the mask layer 20 to prevent migration of those materials from the clear coat layer 22 during a thermoforming or molding process. For example, triazoles, such as benzotriazole, triazines and benzophenone may be added to the mask layer 20. Specific examples of these types of additives include TINUVIN 1130 and TINUVIN 292, both manufactured  
20 by Ciba Geigy of Hawthorne, NY.

Lubricants, release agents, surfactants, and slip additives may also be added to the mask layer 20. For example, release agents, such as silicones and waxes, may be added to the mask layer 20 so that at least a portion of the release agent migrates into the clear coat 22. The release agent reduces the coefficient of  
25 friction of the outer surface of the paint film 18 so that the paint film is less prone to scratching and marring. Application of heat and/or pressure to the paint film 18 also causes a portion of the release agent to migrate to the outer, exposed surface of the mask layer 20. As a result, the outer surface of the mask layer 20 also exhibits a reduced coefficient of friction. A specific example of a silicone  
30 additive is BYK333 manufactured by BYK Chemie of Wallingford, CT.

In another embodiment, certain types of additives, such as plasticizers, are added to the clear coat layer 22 and encouraged to migrate into the mask layer 20

during a thermoforming or molding process in order to remove the additives from the clear coat layer of the final product. For example, plasticizers may be helpful in improving elongation of the clear coat layer 22 for thermoforming, but detrimental to the long-term performance of the paint film 18. Using the mask layer 20 of the present invention, a plasticizer composition may be added to the clear coat layer 22 for improved elongation during thermoforming. The elevated temperature and/or pressure of the thermoforming process causes the plasticizer to migrate into the mask layer 20, thereby obtaining the benefits of the plasticizer without harming the long-term performance of the paint film 18.

Figures 5 and 6 are greatly expanded cross-sectional views of two embodiments of the decorative sheet material 14 of the present invention. The decorative paint film 18 may comprise a single layer 25 of a pigmented polymer, as shown in Figure 6, or may comprise multiple layers, as shown in Figures 4 and 5. If a single layer 25 of pigmented polymer is used, the polymer may be selected from the group consisting of urethane polymers, acrylic polymers, fluoropolymers, and alloys of a fluoropolymer and an acrylic polymer. FLUOREX® films manufactured by Rexam are examples of alloys of a fluoropolymer and an acrylic polymer. The single layer 25 of pigmented polymer may also include UV screeners to enhance weatherability, antioxidants, heat stabilizers, and other conventional additives. The pigmented polymer layer 25 may further include pigments, dyes, and/or flakes to enhance visual appearance.

As shown in Figures 4 and 5, the decorative paint film 18 may also comprise both a clear coat layer 22 and a color coat layer 24. The clear coat layer 22 is formed from a substantially transparent weatherable polymer composition selected to provide a film which will not significantly fade, peel, crack, or chalk when exposed to the environment for the intended life of the part 12. Additionally, the clear coat layer 22 must be formable from a two-dimensional surface to a three-dimensional surface without objectionable loss of appearance or performance properties. Advantageously, the clear coat layer 22 is selected from the group consisting of urethane polymers, acrylic polymers, fluoropolymers, and alloys of a fluoropolymer and an acrylic polymer (such as FLUOREX® films). As with the single pigmented polymer layer 25, the clear

coat layer 22 may include UV screeners, antioxidants, heat stabilizers, and other conventional additives. Preferably, the clear coat layer 22 is about 0.3 to about 3 mils in thickness.

5 The color coat layer 24 is formed of a polymer composition containing a uniformly dispersed pigment to provide the appearance necessary for exterior automobile use. Preferably, the color coat layer 24 is selected from the group consisting of urethane polymers, acrylic polymers, fluoropolymers, and alloys or a fluoropolymer and acrylic polymer (such as FLUOREX® films). The color coat layer 24 may include pigments, dyes, and/or flakes to enhance visual  
10 appearance and improve weatherability. Preferably, the color coat layer 24 is about 0.3 to about 3 mils in thickness.

If desired, a color adjustment layer 27 may be added between the clear coat layer 22 and the color coat layer 24 to enhance visual appearance. The color adjustment layer 27 can be applied in coating form and include pigments, dyes  
15 and/or flakes or applied as a graphic design using printing methods such as gravure, rotary screen, flat bed step-and-repeat screen, ink jet, flexographic or other printing techniques.

The primer layer 26 improves adhesion between the color coat layer 24 and the adhesive layer 28. The primer layer 26 preferably comprises an acrylic polymer prepared in solution using any compatible solvent known in the art, such  
20 as toluene. In one embodiment, the primer layer 26 is prepared from a solution comprising about 65 to about 85 weight percent acrylic composition and about 5 to about 10 weight percent solvent. An acrylic polymer suitable for use in the primer layer 26 is acrylic adhesive 68070 manufactured by DuPont. The primer  
25 layer 26 may be opaque, colored or clear. Opaque is defined as less than 1 percent transmission at a wavelength of less than 400 nm. The primer layer 26 is preferably about 0.2 to about 2 mils in thickness. The primer layer 26 may be colored or opaque to protect the underlying thermoformable backing layer 30 from damage caused by UV exposure. Pigments such as carbon black, titanium  
30 oxide, and mixtures thereof may be added to impart color to the acrylic polymer composition used in the primer layer 26. Additionally, additives such as UV screeners, antioxidants, and heat stabilizers may be added to the primer layer 26.

The adhesive layer 28 adheres the decorative paint film 18 to a thermoformable backing layer 30. The adhesive layer 28 is selected from the group consisting of urethane adhesives, acrylic adhesives, acrylic adhesives with cross linkers, chlorinated polyolefins and mixtures thereof. Preferably, a mixture of a chlorinated polypropylene and a higher molecular weight chlorinated polyolefin is used. In one embodiment, the adhesive layer 28 is formed from a mixture of about 5 to about 20 weight percent chlorinated polypropylene and about 1 to about 10 weight percent of a higher molecular weight chlorinated polyolefin formed in solution. A compatible solvent known in the art, such as toluene, is present in an amount of about 60 to about 80 weight percent. A chlorinated polypropylene suitable for use with the present invention is HARDLEN 13LP manufactured by Advanced Polymer. A higher molecular weight chlorinated polyolefin suitable for use with the present invention is SUPERCHLON 822S manufactured by CP/Phibrochem of Fort Lee, NJ. The adhesive layer 28 should be capable of stretching about 300 to about 600 percent. Due to the substantial elongation capability of the adhesive layer 28, the adhesive layer maintains the necessary adhesive strength to prevent delamination of the decorative paint film 18 from the thermoformable backing layer 30 over a wide temperature range.

An epoxy component, such as EPON 828RS manufactured by Shell Chemical, may be added in small amounts (approximately about 0.1 to about 2.0 weight percent on a dry solids basis) as an acid scavenger. As with the primer layer 26, the adhesive layer 28 may be colored or opaque to protect the underlying thermoformable backing layer 30 from damage caused by UV exposure. Pigments such as carbon black, titanium oxide, and mixtures thereof may be added to impart color to the polymer composition used in the adhesive layer 28. Additives such as UV screeners, antioxidants, and heat stabilizers may be added to the adhesive layer 28. Preferably, the adhesive layer 28 is about 0.2 to about 2 mils in thickness.

The thermoformable backing layer 30 bonds the decorative paint film 18 of the decorative sheet material 14 to the substrate 16. In addition, the backing layer 30 provides bulk and/or rigidity for handling the decorative sheet material

14 as a thermoformed preform. The backing layer 30 also provides thickness to prevent glass fibers, fillers or other sources of visual roughening or "orange peel" from the substrate 16 from affecting the visual appearance of the decorative sheet material 14. The backing layer 30 must bond well with both the substrate 16 and the adhesive layer 28. The backing layer 30 may be selected from the group consisting of thermoplastic olefin, acrylonitrile-butadiene-styrene terpolymer, polypropylene, thermoplastic polyimide, polyethylene oxide, polycarbonate, polyvinyl chloride, polystyrene, styrene/polyphenylene oxide (NORYEL), polybutylene terephthalate, nylon, PETG copolyester, and mixtures, laminates and copolymers thereof, depending on the material used as the substrate 16.

Figure 7 illustrates a process for constructing the decorative sheet material 14 of the present invention. As shown, a film carrier 33 is advanced from a supply roll 38 through a series of process steps. The film carrier 33 preferably comprises a polyester casting film having a high gloss surface. The film carrier 33 is important for high gloss applications because it imparts high gloss and DOI to the decorative sheet material 14. Advantageously, the film carrier 33 comprises polyethylene terephthalate (PET) in a grade without slip additives. The film carrier 33 is about 1 to about 3 mils in thickness, preferably about 2 mils in thickness.

The film carrier 33 passes through a first coating station 40. If a single pigmented layer 25 is used as the decorative paint film 18, the pigmented layer is deposited onto the film carrier 33 using coating station 40 and the resulting film is dried by dryer 46. If a decorative paint film 18 having multiple coatings is desired, the first coating station 40 may deposit the clear coat layer 22. The clear coat layer 22 then passes through a dryer 42. Thereafter, a color coat layer 24 is deposited on the dried clear coat layer 22 using coating station 44. The color coat layer 24 is then dried using dryer 46. Optionally, the dried color coat layer 24 can be subjected to a corona treatment (not shown).

The coating stations 40 and 44 may utilize any conventional coating or casting techniques, such as reverse roll coating or slot die coating techniques. Slot die coating methods are preferred.

The dryers 42 and 46 may utilize any conventional drying technique. Preferably the dryers 42 and 46 are ovens having multiple heating zones wherein each successive heating zone operates at a progressively higher temperature. For example, an oven having four to six heating zones ranging in temperature from about 200 F to about 400 F may be used. Alternatively, dryer 42 may be eliminated from the process such that the color coat 24 is applied to the clear coat 22 while the clear coat is still wet.

After the decorative paint film 18 is applied to the film carrier 33, the film carrier advances to a primer coating station 48, where the primer layer 26 is deposited onto the exposed layer of the decorative paint film 18. The primer layer 26 is then dried using dryer 49. Thereafter, the film carrier advances to an adhesive coating station 50, where the adhesive layer 28 is deposited onto the primer layer 26. Thereafter, the adhesive layer 28 is dried using dryer 51. The primer coating station 48 and adhesive coating station 50 may utilize any conventional coating or casting technique, such as reverse roll coating or slot die coating techniques. The dryers 49 and 51 may utilize any conventional drying technique.

A thermoformable backing layer 30 is advanced from a supply roll 52 and laminated to the adhesive-coated surface of the film carrier 33. Optionally, the backing layer 30 can be subjected to a corona treatment (not shown) prior to lamination. The resulting laminate is collected by product roll 54.

Figure 8 illustrates a process for preparing a decorative sheet material 14 having a mask layer 20. A non-extensible carrier 34 is advanced from a supply roll 58. The carrier 34 may be constructed of the same material used for the film carrier 33. Preferably, the carrier 34 comprises a polyethylene terephthalate film. The carrier 34 advances through a coating station 60, where the mask layer 20 is deposited onto a surface of the carrier. The coating station 60 may utilize any coating or casting technique known in the art, such as reverse roll coating or slot die coating techniques. Thereafter, the coated carrier 34 passes through a dryer 62 to form a dried mask layer 20. As discussed above in connection with dryers 42 and 46 used to dry the decorative paint film 18, the dryer 62 used to dry the mask layer 20 may utilize any conventional drying technique. Preferably, the

dryer 62 comprises an oven with multiple heating stages. The dryer 62 evaporates the solvents present in the mask layer 20 composition.

The layers of the decorative sheet material 14 formed in the process illustrated in Figure 7 are advanced from a supply roll 56. The film carrier 33 is  
5 stripped away from the remaining layers to expose either the single pigmented layer 25 or the clear coat layer 22 of the decorative paint film 18, depending on the construction of the paint film used. The exposed outer layer of the decorative paint film 18 is laminated and releasably bonded to the mask layer 20 by nipping the two films between two rollers, 64 and 65, with or without applying heat to the  
10 layers. The resulting decorative sheet material 14 is collected by product roll 67. The non-extensible carrier 34 may be stripped away to expose the mask layer 20 before or after collection of the sheet material 14 by product roll 67.

In another embodiment, the decorative paint film 18, primer layer 26, and adhesive layer 28 are coated directly onto the dried mask layer 20 rather than  
15 laminating the coated films together. In a further embodiment, the mask layer is coated onto the clear coat layer 22. For example, a decorative sheet material 14 prepared according to Figure 7 could be stripped from carrier 33 so that the mask layer 20 can be coated directly onto the clear coat layer 22.

The decorative sheet material 14 of the present invention can be adhered  
20 to a supporting substrate 16 in accordance with known laminating or bonding techniques. Illustrative examples of supporting substrates 16 include metal, wood, and molded polymer substrates. As explained above, exterior automobile parts are particularly suitable as the substrate 16. Suitable polymers for use as the substrate 16 include, for example; thermoplastic olefin, acrylonitrile-butadiene-  
25 styrene terpolymer, polypropylene, thermoplastic polyimide, polyethylene oxide, polycarbonate, polyvinyl chloride, polystyrene, styrene/polyphenylene oxide (NORYEL), polybutylene terephthalate, nylon, PETG copolyester, Sheet Molding Compounds (SMC), RIM urethanes, and mixtures, laminates and copolymers thereof.

30 The decorative sheet material 14 may be applied to the substrate 16 by a variety of methods. These methods include, but are not limited to, compression molding, such as thermoplastic or thermoset compression molding, injection



molding and the like. In an injection molding process, the decorative sheet material 14 may be preformed as described below or placed in the mold as a substantially flat sheet. If the sheet material 14 is placed in the mold without preforming, the heat and/or pressure of the molding process conforms the sheet material to the desired shape.

Figures 9A-9D illustrate the steps in a thermoforming process. Thermoforming is often used to create a preform in a three-dimensional configuration that roughly approximates the three-dimensional configuration of the final product. The preform is then placed in a mold for in-mold surfacing of a desired substrate 16 to form the final product. Figure 9A shows heating of the decorative sheet material 14 of the present invention by heating elements 70. The heating step softens and increases the extensibility of the decorative sheet material 14 so that the sheet material will readily conform to the contoured outer surface of the mold 74. As shown in Figure 9C, the mold 74 is brought into contact with the heated decorative sheet material 14 and a vacuum is drawn to encourage conformity of the sheet material 14 to the contours of the mold 74. Thereafter, the mold 74 is removed from the decorative sheet material 14 and the sheet material is allowed to cool and harden into the three-dimensional configuration.

Figures 10A-10C illustrate steps in an in-mold surfacing process. As shown in Figure 10A, the thermoformed decorative sheet material 14 is placed in the mold cavity 78 of an injection mold 76. The decorative sheet material is placed in the mold cavity 78 with the mask layer 20 facing the inner surface of the injection mold 76. Alternatively, the decorative sheet material 14 may be placed in the mold cavity 78 as a flat, two-dimensional insert rather than as a preform. As noted above, the mold 76 may have a roughened inner surface. The injection mold 76 is shut and a moldable polymer 82 is introduced into the mold 76 through the injection mold barrel 80. The polymer 82 bonds to the backing layer 30 and conforms to the contoured shape of the mold cavity 78. Thereafter, the moldable polymer 82 is allowed to cool and harden into a composite shaped part 12 comprising a substrate 16 bonded to a decorative sheet material 14, as shown in Figure 10C. The mask layer 20 of the decorative sheet material may be

stripped from the composite shaped part 12 to expose the paint film finish when desired.

#### EXAMPLE 1

The data in Table 1 illustrates the migration of ultraviolet light stabilizer from the clear coat to the mask layer that can occur if no UV light stabilizer is present in the mask layer. The percent transmission (%T) of UV light and visible light (from 280 nm to 480 nm) of the mask layer was measured before and after thermoforming a sample of the decorative sheet material of the present invention. No UV light stabilizer was present in the mask composition prior to thermoforming. The data clearly shows absorption of certain wavelengths by the mask layer after thermoforming, indicating that UV light stabilizer migrated from the clear coat layer to the mask layer.

Table 1

Wavelength	%T Mask before forming	%T Mask after forming
280	0	0
300	70	45 >
320	88	52 >
340	90	48
360	90	50
380	90	70
400	90	90
420	90	90
440	90	90
460	90	90
480	90	90

## EXAMPLE 2

A green metallic paint film was thermoformed with a mask layer of the present invention that contained TINUVEN 1130 and TINUVIN 292. The same paint film was thermoformed with a mask layer that did not contain any UV additives and also thermoformed without any mask layer. The paint film was a base coat/ clear coat film constructed as described herein. The three samples were stretched to 100% elongation by thermoforming and UV scans were conducted on a Beckmann DU-7 spectrophotometer. The results are recorded in Table 2. The results indicate that addition of the UV additives to the mask layer of the present invention inhibited migration of UV additives from the paint film into the mask layer. The paint film thermoformed with a mask layer having UV additives showed less transmission of UV light than the paint film thermoformed with a mask layer without UV additives, indicating greater retention of UV additives in the paint film.

Table 2  
% Transmission

SAMPLE	300 nm	320 nm	340 nm	360 nm
Paint Film with mask and UV additives	0.00	0.20	0.10	0.30
Paint Film with mask – no UV additives	0.20	0.50	0.30	0.60
Paint Film without mask	0.00	0.20	0.10	0.20

## EXAMPLE 3

Paint films were prepared according to the present invention. The paint films were constructed both with and without a mask layer. A 195.6 gram wt assembly with a polyamide surface was placed horizontally on the surface of each paint film. A wire was attached to the wt assembly and the assembly was pulled across the surface of each paint film. The other end of the wire was attached to either an Instron or Sintech pull tester and force readings were collected as the assembly traveled across the paint film surface. Lower coefficient of friction (COF) readings indicate better gouge resistance. As the data indicates, addition of the slip additive to the mask layer results in migration of the additive to the paint film. The migration of the additive leads to a decrease in the COF of the underlying paint film.

Table 3 lists the COF data measured using an Instron Pull Tester. All samples were thermoformed. The mask layer referred to in Table 3 contained 1.5% BYK-333 slip additive.

Table 4 lists the COF data measured using a Sintech Pull Tester. All samples were thermoformed. The mask layer referred to in Table 4 contained 0.5% BYK-333. Readings were collected both before and after removal of the mask layer.

Table 3

Paint Film Color	COF Reading
White - No mask	0.61, 0.66, 0.64
Green - No mask	0.64, 0.64, 0.64
Tan - No mask	0.66, 0.66, 0.66
Tan - With mask *	0.28, 0.28, 0.31
*mask removed for readings	

Table 4

Paint Film Color	COF Reading
Tan - No mask	.51
Tan - With mask on	.30
Tan - With mask off	.39

## EXAMPLE 4

- This example illustrates transfer of a slip additive during a thermoforming operation. A mask layer with slip additive BYK-333 was laminated to the surface of a tan metallic paint film using three temperatures at the lamination nip.
- 5 The mask was then removed and COF readings were taken both before and after removal of the mask layer. The same construction was then laminated and thermoformed at 340°F at various levels of stretch. COF readings were again recorded after thermoforming. The data collected are listed in Table 5. As indicated by the readings below, the paint film exhibited a progressively lower
- 10 COF as stretching during thermoforming increased.

Table 5

Lamination Temp	Mask On	Mask Off	Thermoformed?
300°F	.41	.48	NO
345°F	.41	.48	NO
375°F	.38	.45	NO
375°F-50% stretch	.23	.39	YES-340°F
375°F-150% stretch	.23	.37	YES-340°F
375°F-250% stretch	.21	.34	YES-340°F

- Many modifications and other embodiments of the invention will come to
- 15 mind to one skilled in the art to which this invention pertains having the benefit of the teachings presented in the foregoing descriptions and the associated drawings. Therefore, it is to be understood that the invention is not to be limited to the specific embodiments disclosed and that modifications and other
- embodiments are intended to be included within the scope of the appended
- 20 claims. Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation.

## THAT WHICH IS CLAIMED:

1. A flexible, weatherable decorative sheet material useful in lieu of painting for providing a decorative finish for parts, comprising:
  - a decorative paint film, said paint film having an inner surface and a weatherable outer surface suitable for forming an exterior finish for a part, such as an automobile body part, and
  - an extensible mask releasably adhered to said outer surface of said paint film to form a protective film overlying said paint film, said mask comprising a film-forming polymer composition containing at least one migratory additive.
2. A sheet material according to Claim 1, wherein said at least one migratory additive is selected from the group consisting of hardness enhancers, release agents, ultraviolet light stabilizers, antioxidants, dyes, lubricants, surfactants, catalysts, slip additives and mixtures thereof.
3. A sheet material according to Claim 2, wherein said at least one additive is a hardness enhancer, said hardness enhancer comprising a cross-linking agent.
4. A sheet material according to Claim 3, wherein said cross-linking agent is selected from the group consisting of melamine and polyisocyanate.
5. A sheet material according to Claim 2, wherein said at least one migratory additive is a dye, said dye comprising a fluorescing agent.
6. A sheet material according to Claim 2, wherein said at least one migratory additive is a dye, said dye printed on said mask layer in the form of a graphic design.
7. A sheet material according to Claim 6, wherein said dye is printed on the mask layer using a process selected from the group consisting of gravure, rotary screen, flat bed step-and-repeat screen, ink jet, and flexographic printing techniques.

8. A sheet material according to Claim 2, wherein said at least one migratory additive is a ultraviolet light stabilizer, said ultraviolet light stabilizer selected from the group consisting of triazoles, triazines and benzophenone.
9. A sheet material according to Claim 8, wherein said ultraviolet light stabilizer comprises benzotriazole.
10. A sheet material according to Claim 2, wherein said at least one migratory additive is a release agent, said release agent selected from the group consisting of waxes and silicones.
11. A sheet material according to Claim 10, wherein said release agent is a silicone.
12. A sheet material according to Claim 2, wherein said at least one additive comprises a catalyst, said catalyst comprising para-toluenesulfonic acid.
13. A sheet material according to Claim 1, wherein said at least one migratory additive includes at least one benzotriazole ultraviolet light stabilizer and at least one hindered amine ultraviolet light stabilizer.
14. A sheet material according to Claim 1, wherein said extensible mask comprises a polymer composition selected from the group consisting of polyurethane, polyolefin, polyester and polyamide.
15. A sheet material according to Claim 1, wherein said extensible mask has a thickness of about 0.3 mil to about 3 mils.
16. A sheet material according to Claim 1, additionally including a non-extensible carrier layer releasably adhered to said extensible mask.
17. A sheet material according to Claim 16, wherein said non-extensible carrier layer comprises a polyethylene terephthalate film.
18. A sheet material according to Claim 1, wherein said paint film comprises a single layer of a pigmented polymer.

19. A sheet material according to Claim 1, wherein said paint film comprises a clear coat layer of a transparent weatherable polymer forming said outer surface and an underlying color coat layer of a pigmented polymer forming said inner surface of the paint film.
- 5 20. A sheet material according to Claim 1, further including a thermoformable backing layer bonded to said inner surface of said paint film.
21. A sheet material according to Claim 20, wherein said thermoformable backing layer is selected from the group consisting of thermoplastic olefin, acrylonitrile-butadiene-styrene terpolymer, polypropylene, thermoplastic polyimide, 10 polyethylene oxide, polycarbonate, polyvinyl chloride, polystyrene, styrene/polyphenylene oxide, polybutylene terephthalate, nylon, PETG copolyester, and mixtures, laminates and copolymers thereof.
22. A sheet material according to Claim 20, further comprising an adhesive layer affixing said paint film to said thermoformable backing layer.
- 15 23. A sheet material according to Claim 22, wherein said adhesive layer comprises one or more layers selected from the group consisting of urethane adhesives, chlorinated polyolefins, acrylic adhesives, and mixtures thereof.
24. A preform for in-mold surfacing of a part, such as an automobile part, said preform comprising the sheet material according to Claim 1 which has been 20 heated and formed into a three-dimensional configuration, and wherein said at least one migratory additive composition is present on said outer surface of said paint film.
25. A composite shaped part comprising the preform according to Claim 24, and a substrate of a thermoplastic polymer conforming to the three dimensional configuration of said preform and adhered thereto.
- 25 26. A flexible, weatherable decorative sheet material useful in lieu of painting for providing a decorative finish for parts, comprising:  
a decorative paint film, said paint film having an inner surface and a weatherable outer surface suitable for forming an exterior finish for a part, such as an



automobile body part, said outer surface having a 60 degree gloss value of at least 65, and

an extensible mask having inner and outer surfaces, the inner surface being releasably adhered to said outer surface of said paint film to form a protective film overlying said paint film, said extensible mask comprising a urethane polymer composition containing at least one migratory additive selected from the group consisting of hardness enhancers, release agents, ultraviolet light stabilizers, antioxidants, dyes, lubricants, surfactants, catalysts, slip additives and mixtures thereof.

27. A sheet material according to Claim 26, wherein said at least one migratory additive includes a ultraviolet light stabilizer, said ultraviolet light stabilizer selected from the group consisting of triazoles, triazines and benzophenone.

28. A sheet material according to Claim 26, wherein said at least one migratory additive includes a release agent, said release agent selected from the group consisting of waxes and silicones.

29. A sheet material according to Claim 26, wherein said at least one migratory additive includes at least one benzotriazole ultraviolet light stabilizer and at least one hindered amine ultraviolet light stabilizer.

30. A sheet material according to Claim 26, further including a thermoformable backing layer adhered to said inner surface of said paint film, and an adhesive layer adhering said paint film to said thermoformable backing layer.

31. A flexible, weatherable decorative sheet material useful in lieu of painting for providing a decorative finish for parts, comprising:

a decorative paint film, said paint film having an inner surface and a weatherable outer surface suitable for forming an exterior finish for a part, such as an automobile body part, said outer surface having a 60 degree gloss value of at least 65, and said paint film comprising at least one layer which contains a weatherable alloy of a fluoropolymer composition and an acrylic polymer composition,

an extensible mask having inner and outer surfaces, the inner surface being releasably adhered to said outer surface of said paint film to form a protective

film overlying said paint film, said extensible mask comprises a urethane polymer film having dispersed therein least one migratory additive composition selected from the group consisting of hardness enhancers, release agents, ultraviolet light stabilizers, antioxidants, dyes, lubricants, surfactants, catalysts, slip additives and mixtures thereof;

an adhesive layer overlying said inner surface of said paint film, and a thermoformable backing layer formed of a thermoplastic olefin composition adhered to said inner surface of said paint film by said adhesive layer.

32. A preform for in-mold surfacing of a part, such as an automobile part, to provide a decorative finish for such part, said preform comprising a laminate which has been heated and formed into a three dimensional configuration, said laminate comprising:

a decorative paint film having an inner surface and a weatherable outer surface suitable for forming an exterior finish for a part, such as an automobile body part, and

an extensible mask releasably adhered to said outer surface of said paint film to form a protective film overlying said paint film, said mask comprising a film-forming polymer composition containing at least one migratory additive, said migratory additive being present in said outer surface of said paint film and also being present at the exposed surface of said extensible mask.

33. A preform according to Claim 32, wherein said at least one migratory additive includes a ultraviolet light stabilizer, said ultraviolet light stabilizer selected from the group consisting of triazoles, triazines and benzophenone.

34. A preform according to Claim 32, wherein said at least one migratory additive includes a release agent, said release agent selected from the group consisting of waxes and silicones, said release agent imparting a reduced coefficient of friction to the exposed surface of said extensible mask and to said outer surface of the paint film.

35. A preform according to Claim 32, wherein said at least one migratory additive includes at least one benzotriazole ultraviolet light stabilizer and at least one hindered amine ultraviolet light stabilizer.

36. A method of making a flexible, weatherable decorative sheet material,  
5 comprising:

applying a coating comprising a film-forming polymer containing at least one migratory additive composition onto a casting surface,

drying the coating to form a continuous polymer mask releasably adhered to said casting surface,

10 forming a decorative paint film having an inner surface and an outer surface,

releasably bonding said outer surface of said paint film to the exposed surface of said mask to form a composite laminate, and

15 heating the laminate to effect migration of said migratory additive into said paint film.

37. A method according to Claim 36, further comprising the step of stripping the mask from paint film to expose said outer surface of the paint film.

38. A method according to Claim 36, wherein said step of applying a  
20 coating comprises applying a coating of a urethane polymer composition containing at least one additive selected from the group consisting of hardness enhancers, release agents, ultraviolet light stabilizers, antioxidants, dyes, lubricants, surfactants, catalysts, slip additives and mixtures thereof.

39. A method according to Claim 36, wherein said step of applying a  
25 coating comprises applying a coating of a urethane polymer composition containing at least one ultraviolet light stabilizer, said ultraviolet light stabilizer selected from the group consisting of triazoles, triazines and benzophenone.

40. A method according to Claim 36, wherein said step of applying a  
30 coating comprises applying a coating of a urethane polymer composition containing at least one release agent, said release agent selected from the group consisting of waxes

and silicones, said release agent imparting a reduced coefficient of friction to the outer surface of the paint film.

41. A method according to Claim 36, wherein said step of applying a coating comprises applying a coating of a urethane polymer composition containing at least one benzotriazole ultraviolet light stabilizer and at least one hindered amine ultraviolet light stabilizer.

42. A method according to Claim 36, wherein said step of applying a coating comprises applying a coating of a water-borne polyurethane polymer dispersion onto the casting surface, and said step of drying the polymer coating comprises heating the coating to evaporate the water content.

43. A method according to Claim 36, wherein said step of bonding the mask to the paint film is performed by applying pressure to the layers.

44. A method according to Claim 36, wherein said heating step comprises thermoforming the decorative sheet material into a three dimensional shape while said mask layer remains in place.

45. A method according to Claim 44, further comprising the steps of:  
inserting the thermoformed decorative sheet material into an injection mold with the mask layer facing the mold surface;  
injecting molten thermoplastic polymer into the mold; and  
effecting hardening of the injected thermoplastic polymer to bond the polymer to the decorative sheet material to form a composite shaped part.

46. A method according to Claim 45, further comprising the step of stripping the mask layer from the composite shaped part following said injecting and bonding steps to expose the decorative paint film.

47. A method according to Claim 36, wherein said heating step comprises the steps of:

inserting the decorative sheet material into a mold selected from the group consisting of compression molds and injection molds; and

heating the mold to bond the decorative sheet material to a substrate to form a composite shaped part.

48. A method of making a flexible, weatherable decorative sheet material useful in lieu of painting for providing a decorative finish for parts, comprising:
- 5           applying a coating of a water-borne aliphatic polyurethane polymer composition onto a casting surface, the polymer composition including at least one migratory additive, the migratory additive selected from the group consisting of hardness enhancers, release agents, ultraviolet light stabilizers, antioxidants, dyes, lubricants, surfactants, catalysts, slip additives and mixtures thereof;
- 10           drying the polymer coating to form a continuous extensible aliphatic polyurethane polymer mask layer releasably adhered to said casting surface,
- forming a decorative paint film having an inner surface and a weatherable outer surface suitable for forming an exterior finish for a part, such as an automobile body part, said step of forming a paint film comprising applying at least
- 15           one coating layer to a smooth flexible casting surface, drying said at least one coating layer on said casting surface to produce a paint film with said outer surface releasably bonded to said casting surface and with said inner surface exposed, and bonding the exposed inner surface of said paint film to a thermoformable backing layer,
- stripping said casting surface from said paint film to expose said
- 20           weatherable outer surface of the paint film,
- bringing the exposed weatherable outer surface of the paint film into contact with said mask layer,
- releasably bonding said weatherable outer surface of said paint film to the exposed surface of said mask layer to form a composite laminate; and
- 25           heating the laminate to effect migration of said migratory additive into said paint film.

49. A method of making a flexible, weatherable decorative sheet material useful in lieu of painting for providing a decorative finish for parts, comprising:
- forming a thermoformable decorative paint film having an inner
- 30           surface and a weatherable outer surface suitable for forming an exterior finish for a part, such as an automobile body part, said step of forming a paint film comprising

applying at least one coating layer to a smooth flexible casting surface, drying said at least one coating layer on said casting surface to produce a paint film with said outer surface releasably bonded to said casting surface and with said inner surface exposed, bonding the exposed inner surface of said paint film to a thermoformable backing layer, and stripping said casting surface from said paint film to expose said weatherable outer surface of the paint film,

applying a coating of a polymer to the exposed outer surface of the paint film, the polymer composition including at least one migratory additive, the migratory additive selected from the group consisting of hardness enhancers, release agents, ultraviolet light stabilizers, antioxidants, dyes, lubricants, surfactants, catalysts, slip additives and mixtures thereof, and

drying the polymer coating to form a continuous extensible polymer mask layer releasably bonded to the outer surface of the paint film.

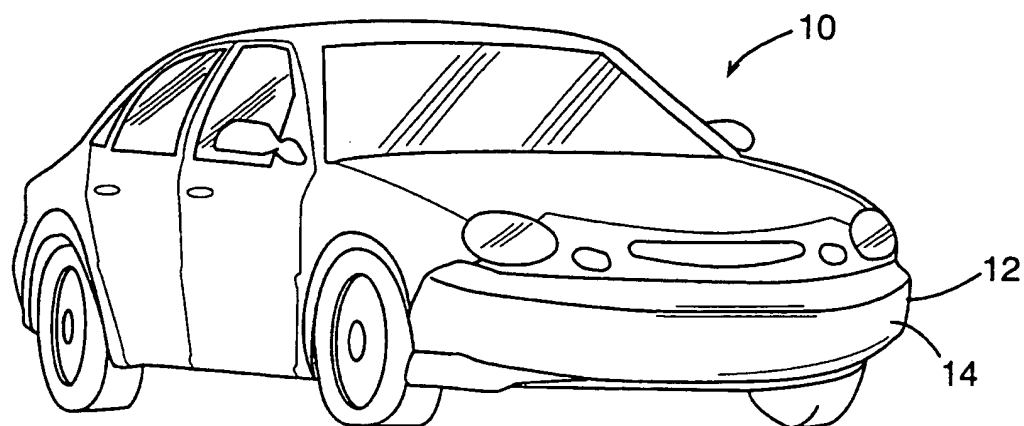
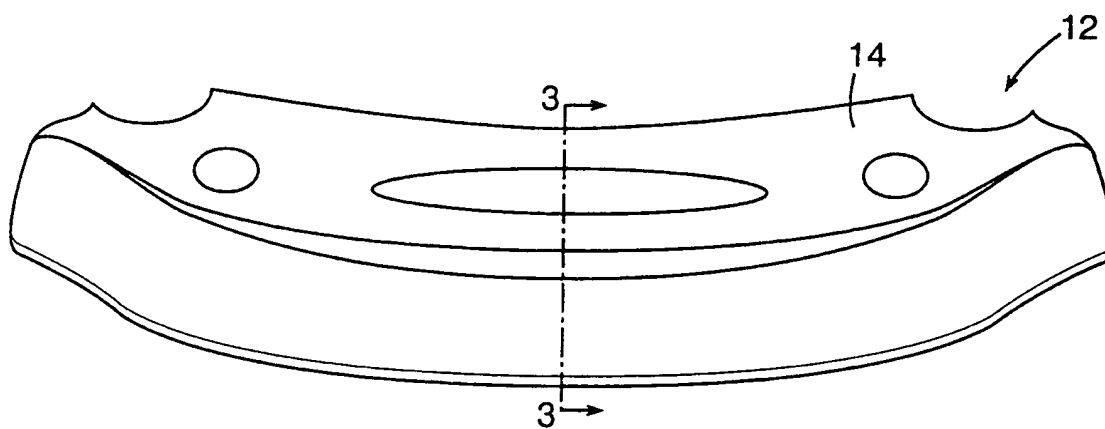
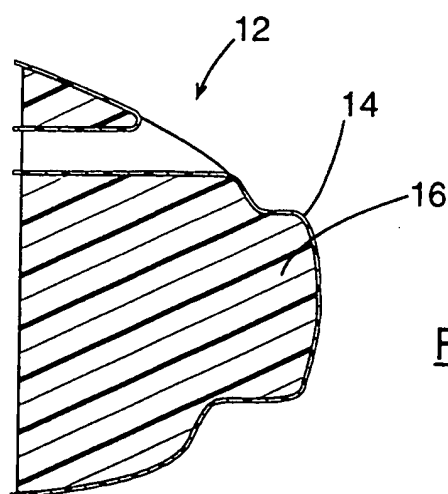
50. A method of making a flexible, weatherable decorative sheet material useful in lieu of painting for providing a decorative finish for parts, comprising:

applying a coating of a polymer onto a casting surface, the polymer composition including at least one migratory additive, the migratory additive selected from the group consisting of hardness enhancers, release agents, ultraviolet light stabilizers, antioxidants, dyes, lubricants, surfactants, catalysts, slip additives and mixtures thereof;

drying the polymer coating to form a continuous extensible polymer mask layer releasably adhered to said casting surface, and

forming a thermoformable decorative paint film having an inner surface and a weatherable outer surface suitable for forming an exterior finish for a part, such as an automobile body part, said step of forming a paint film comprising applying at least one coating layer to the exposed surface of the mask layer, drying said at least one coating layer on said mask layer to produce a paint film with said outer surface releasably bonded to said mask layer and with said inner surface exposed, and bonding the exposed inner surface of said paint film to a thermoformable backing layer.

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FIG. 1.FIG. 2.FIG. 3.

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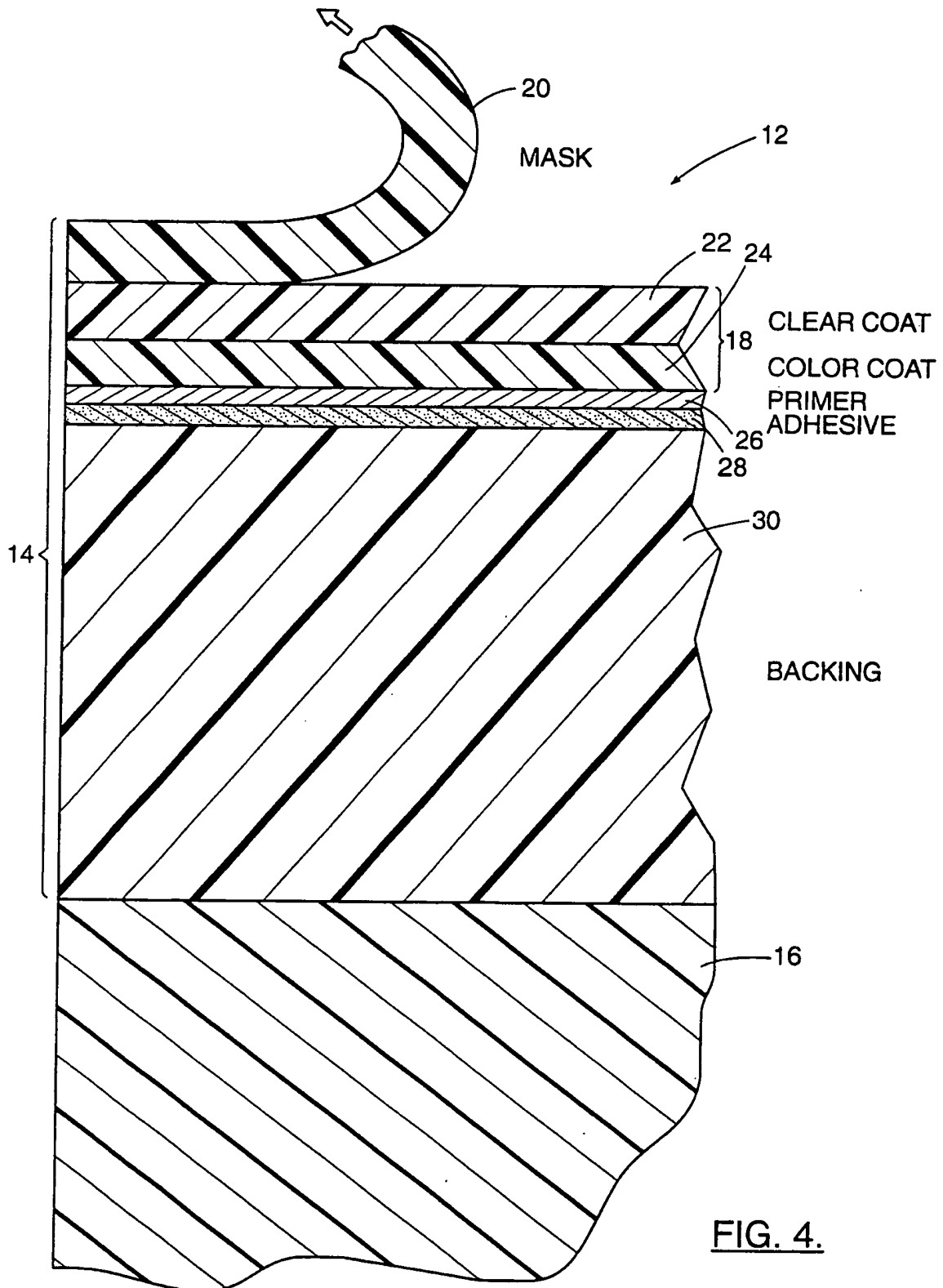
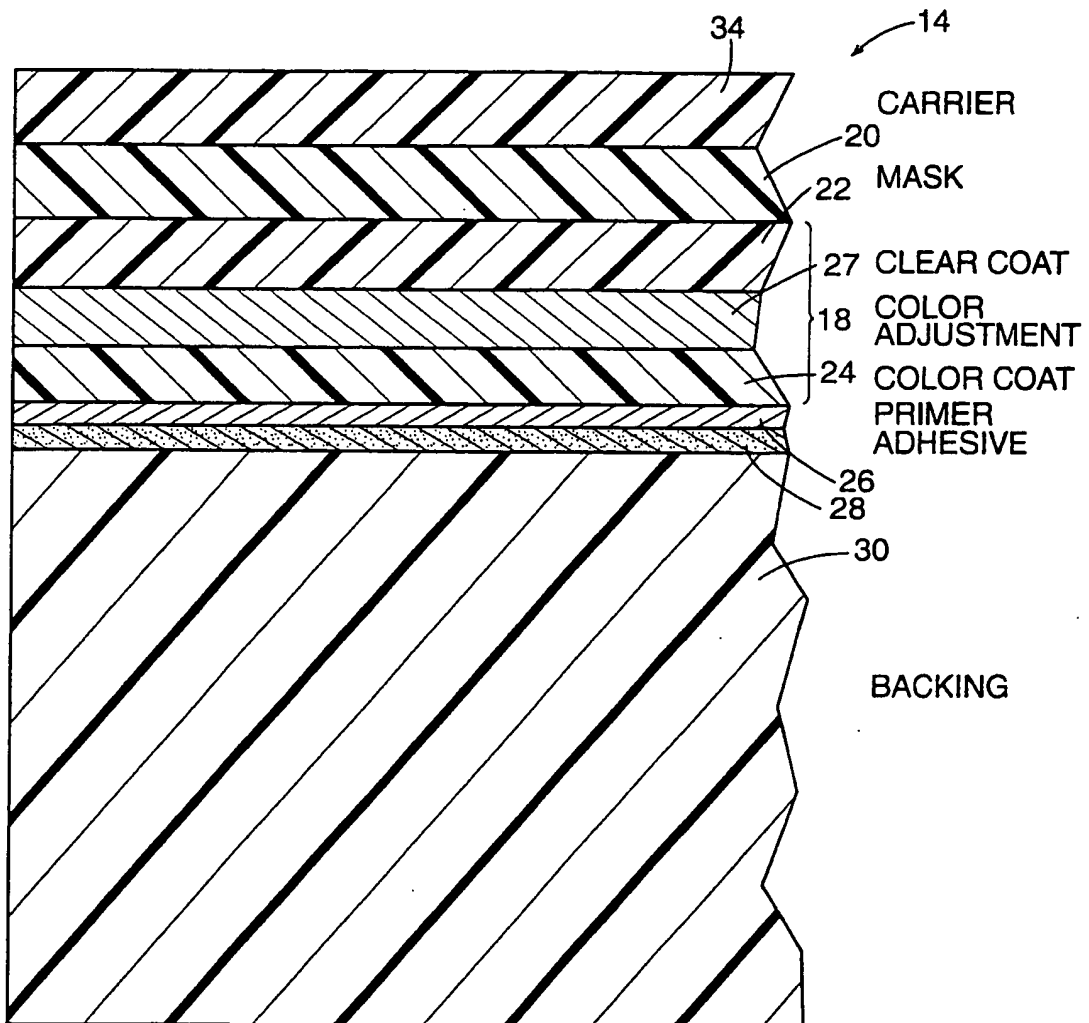


FIG. 4.



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FIG. 5.

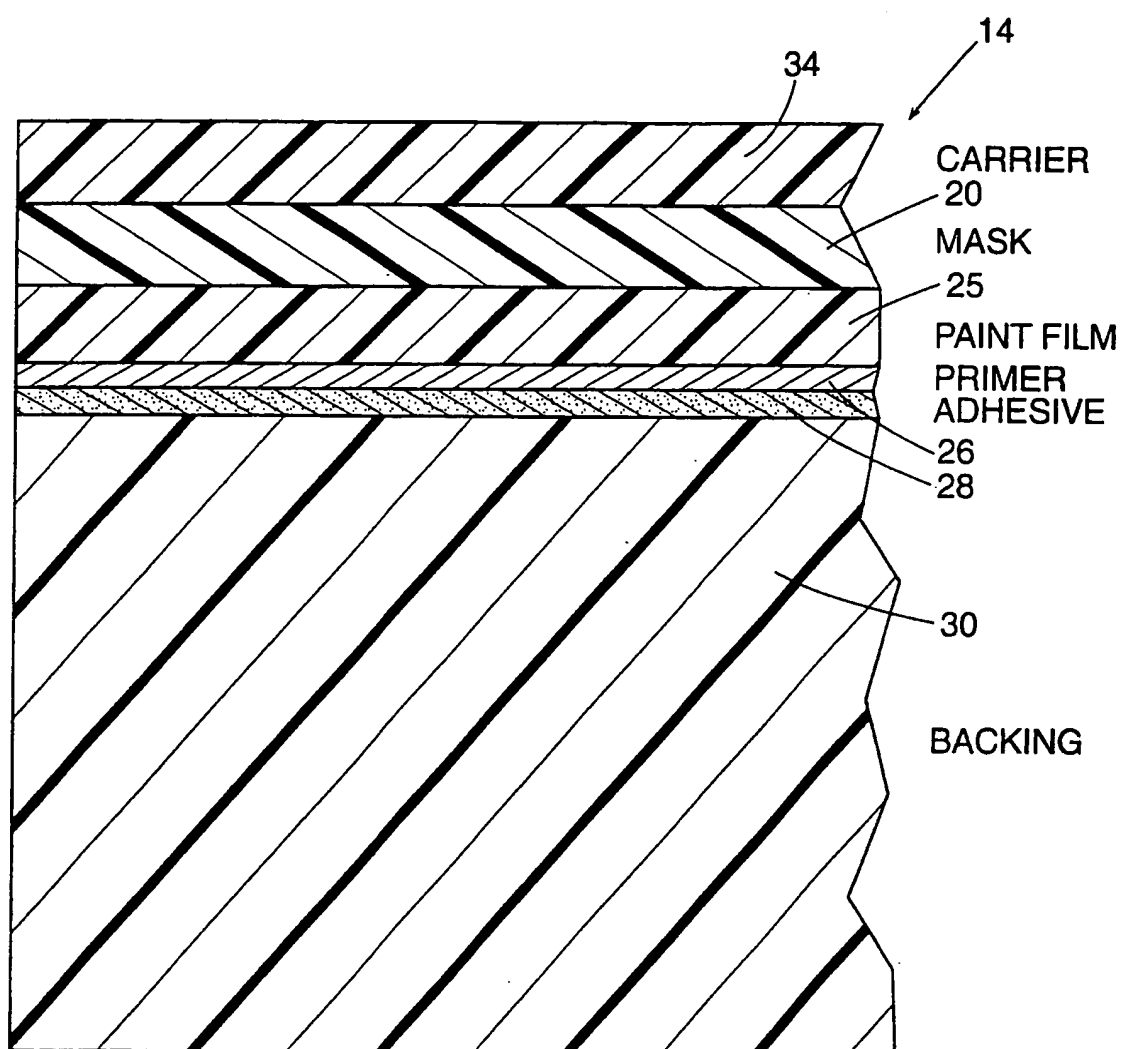


FIG. 6.

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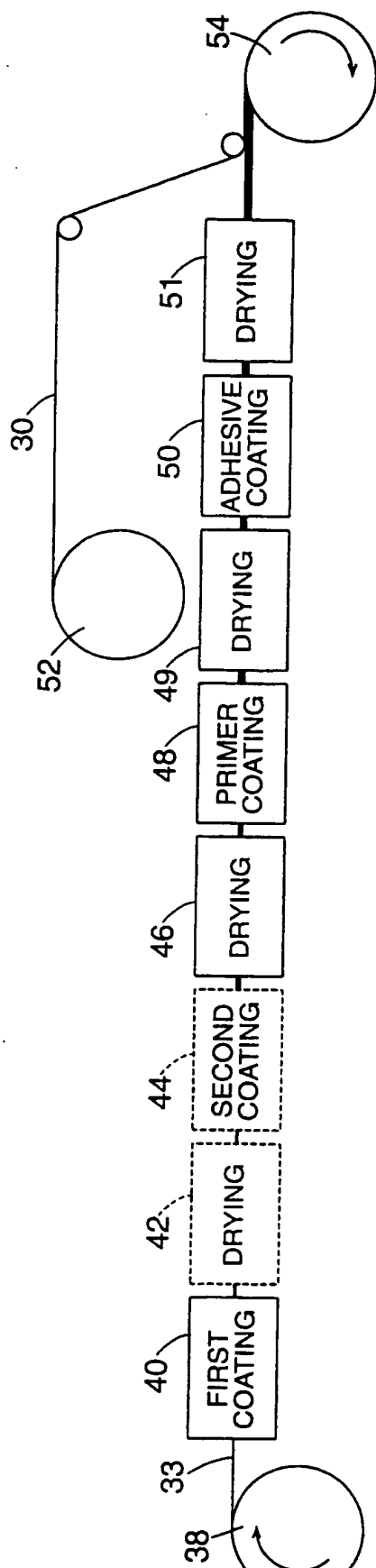


FIG. 7.

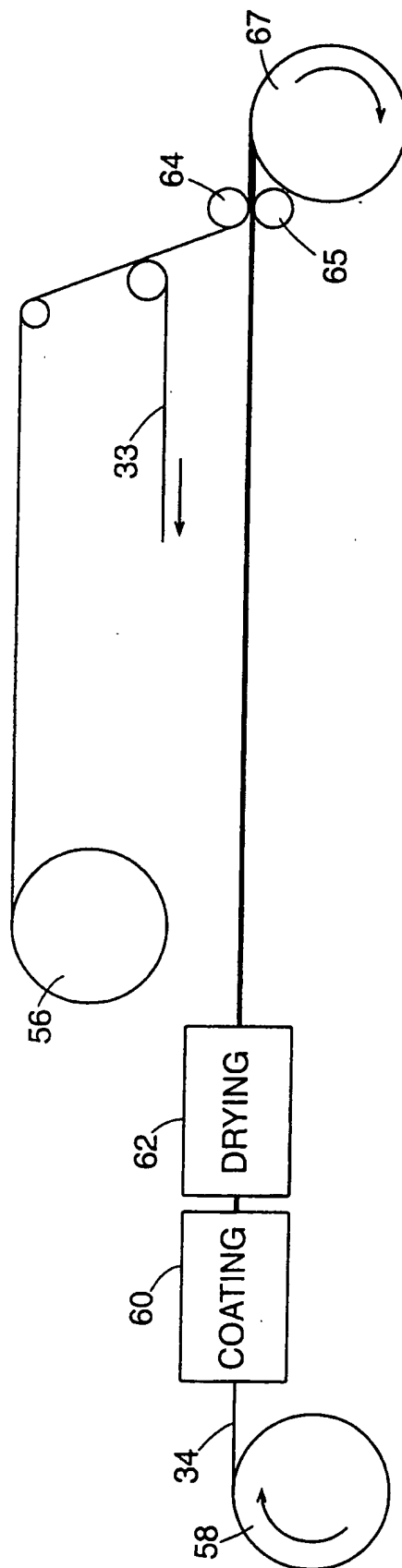


FIG. 8.

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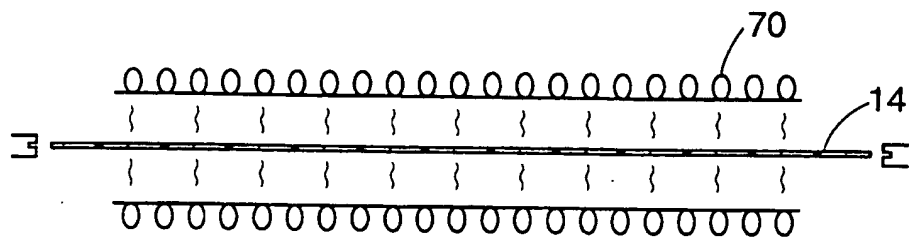


FIG. 9A.

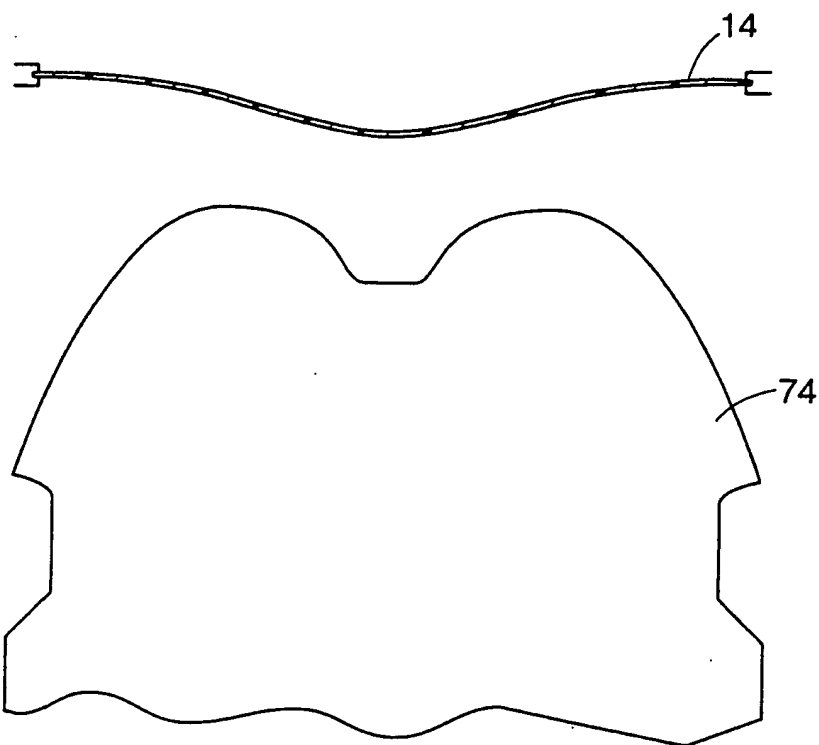


FIG. 9B.

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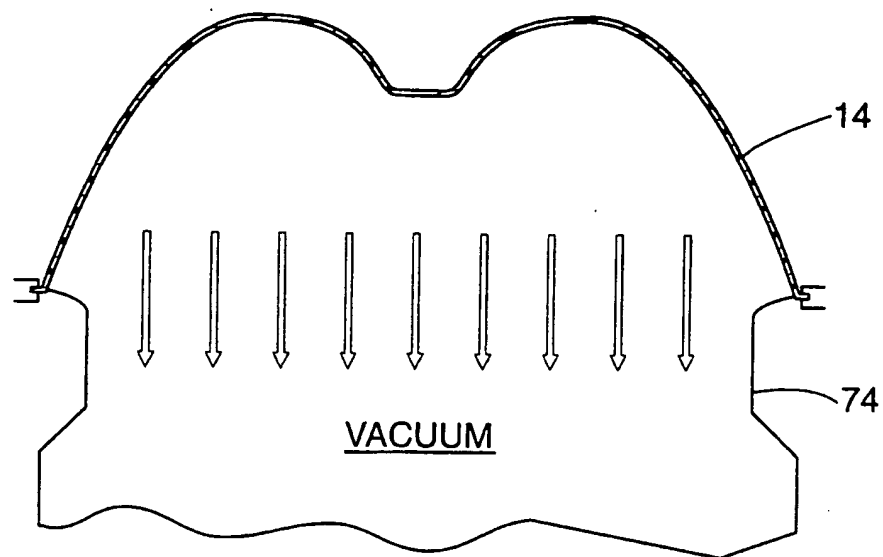


FIG. 9C.

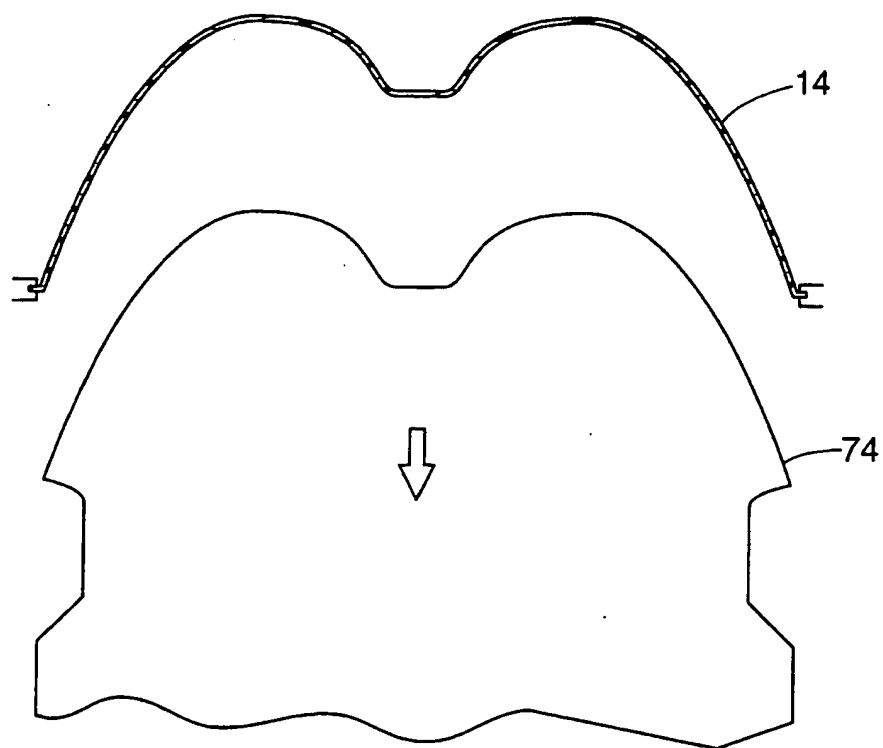
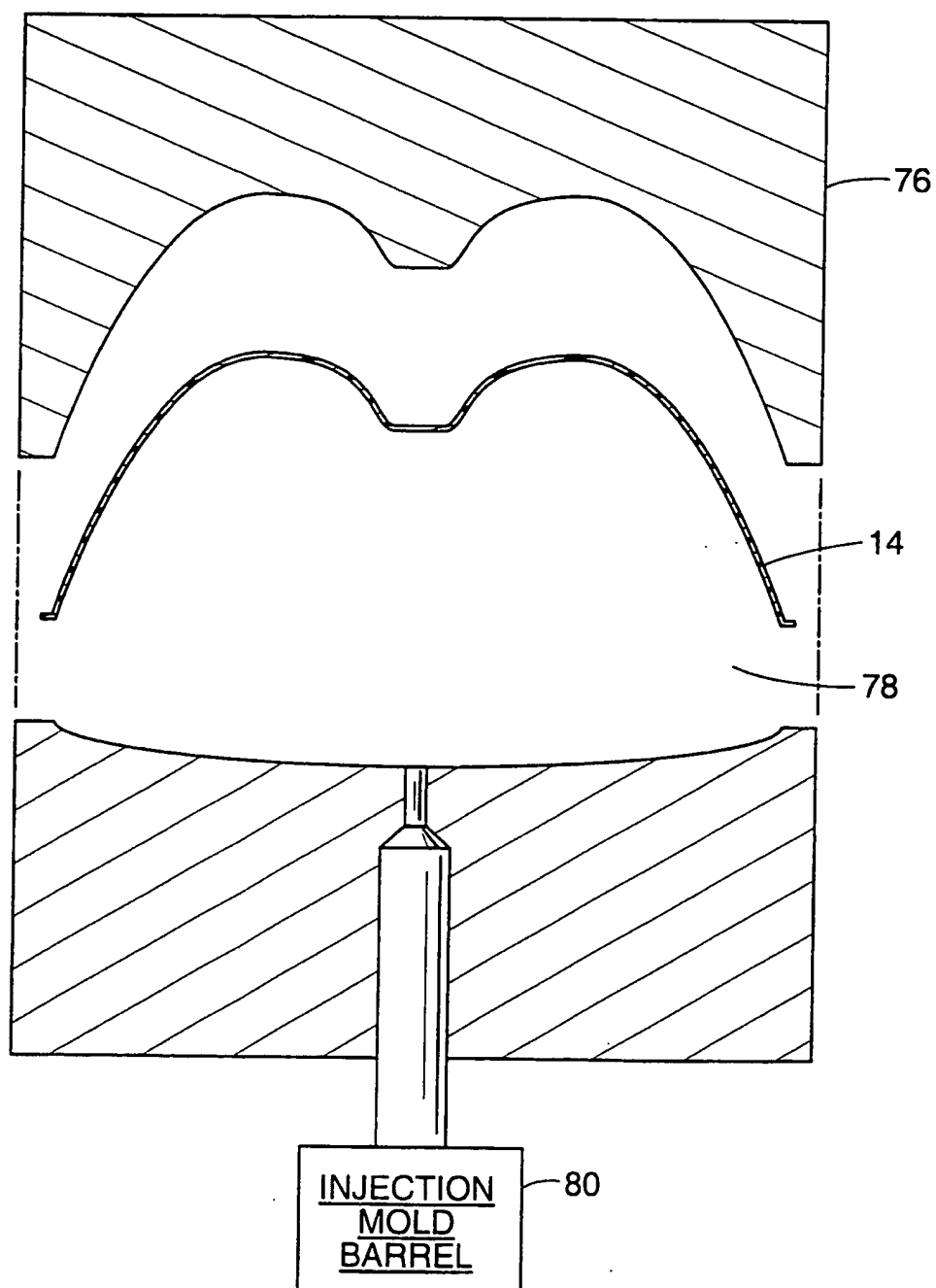


FIG. 9D.

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FIG. 10A.

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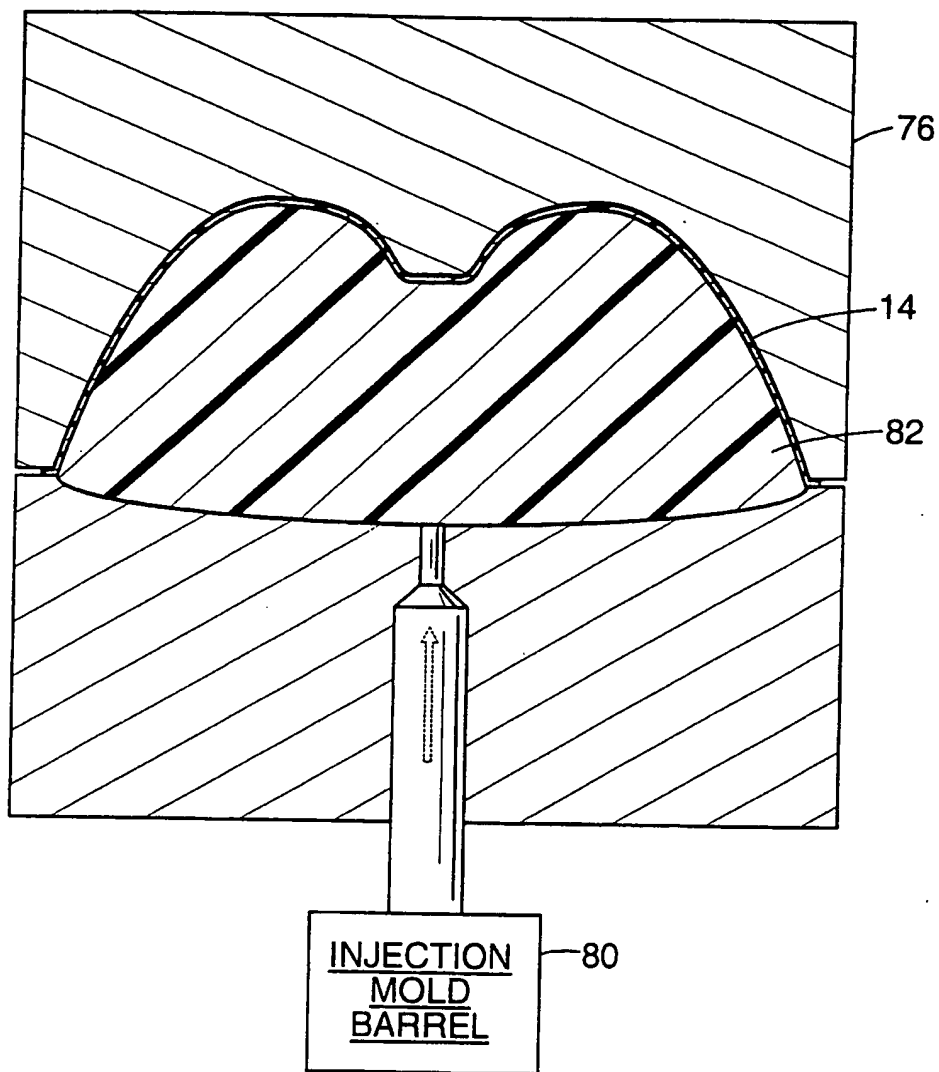


FIG. 10B.

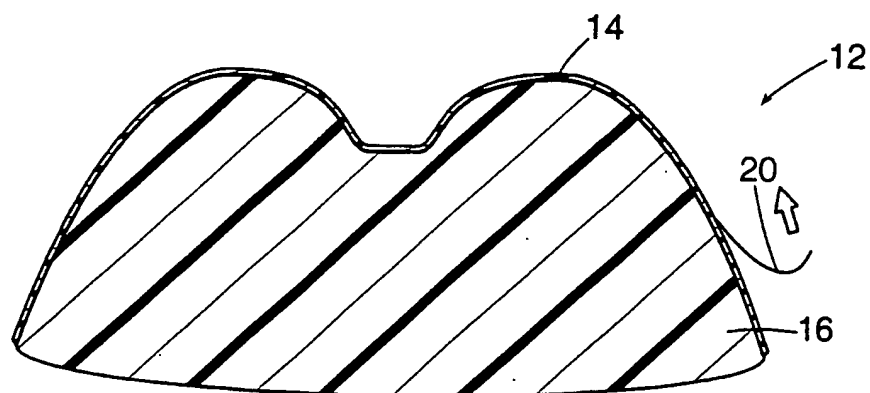


FIG. 10C.

# INTERNATIONAL SEARCH REPORT

Int. onal Application No

PCT/US 00/40003

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B29C37/00 B29C51/16 B29C45/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B29C B44C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 08870 A (MINNESOTA MINING & MFG) 25 February 1999 (1999-02-25)  page 2, line 28 -page 6, line 13 ---	1,24,26, 31,32, 36,48-50
A	WO 94 03337 A (MINNESOTA MINING & MFG) 17 February 1994 (1994-02-17)  page 10, line 15 -page 28, line 20 ---	1,24,26, 31,32, 36,48-50
A	US 5 725 712 A (SPAIN PATRICK LEON ET AL) 10 March 1998 (1998-03-10)  column 4, line 47 -column 6, line 42 --- -/--	1,24,26, 31,32, 36,48-50

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

13 July 2000

Date of mailing of the international search report

04/08/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Herrmann, J



# INTERNATIONAL SEARCH REPORT

Inte. onal Application No

PCT/US 00/40003

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 5 127 974 A (HASHIMOTO SADA AKI ET AL)</p> <p>7 July 1992 (1992-07-07)</p> <p>column 1, line 34 - line 68</p> <p>-----</p>	<p>1, 24, 26,</p> <p>31, 32,</p> <p>36, 48-50</p>

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 00/40003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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